



Sandia National Laboratories

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# XUV absorption in aluminum: Calculating optical properties with electronic structure codes

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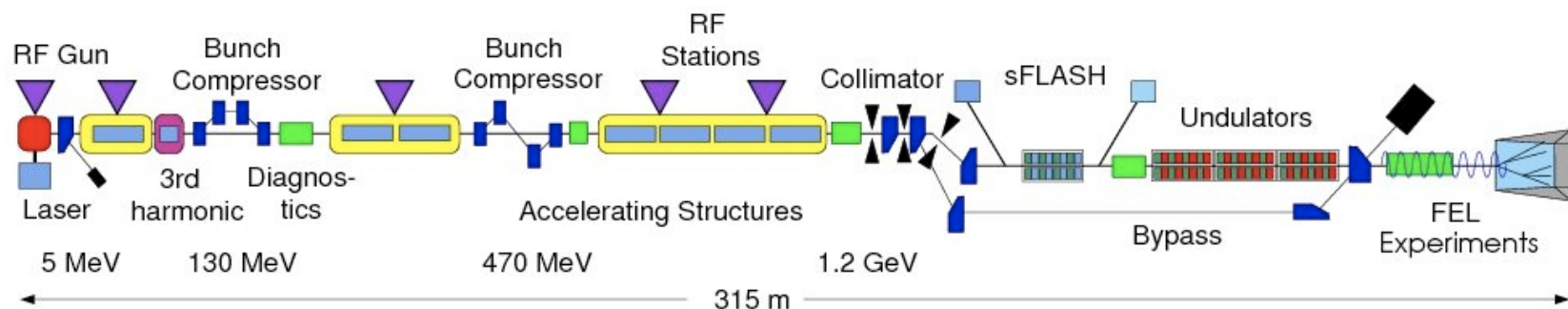
# Acknowledgments

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Department of Physics, Clarendon Laboratory, University of Oxford

Ann Mattsson, Sandia

# The XUV absorption of aluminum is of fundamental and practical interest

- A wide range of free-free dominated absorption
- Excellent test of electronic structure methods
- Practical applications for XUV lithography
- Routine use of Al filters between XUV lasers and spectrometers
- Several frequently cited data sets with unresolved discrepancies
- Well matched to new FEL XUV sources (FLASH at DESY)



Accurate optical properties in general are key to many approaches to temperature measurement

## Several data sets have been generated for absorption in aluminum at ambient conditions

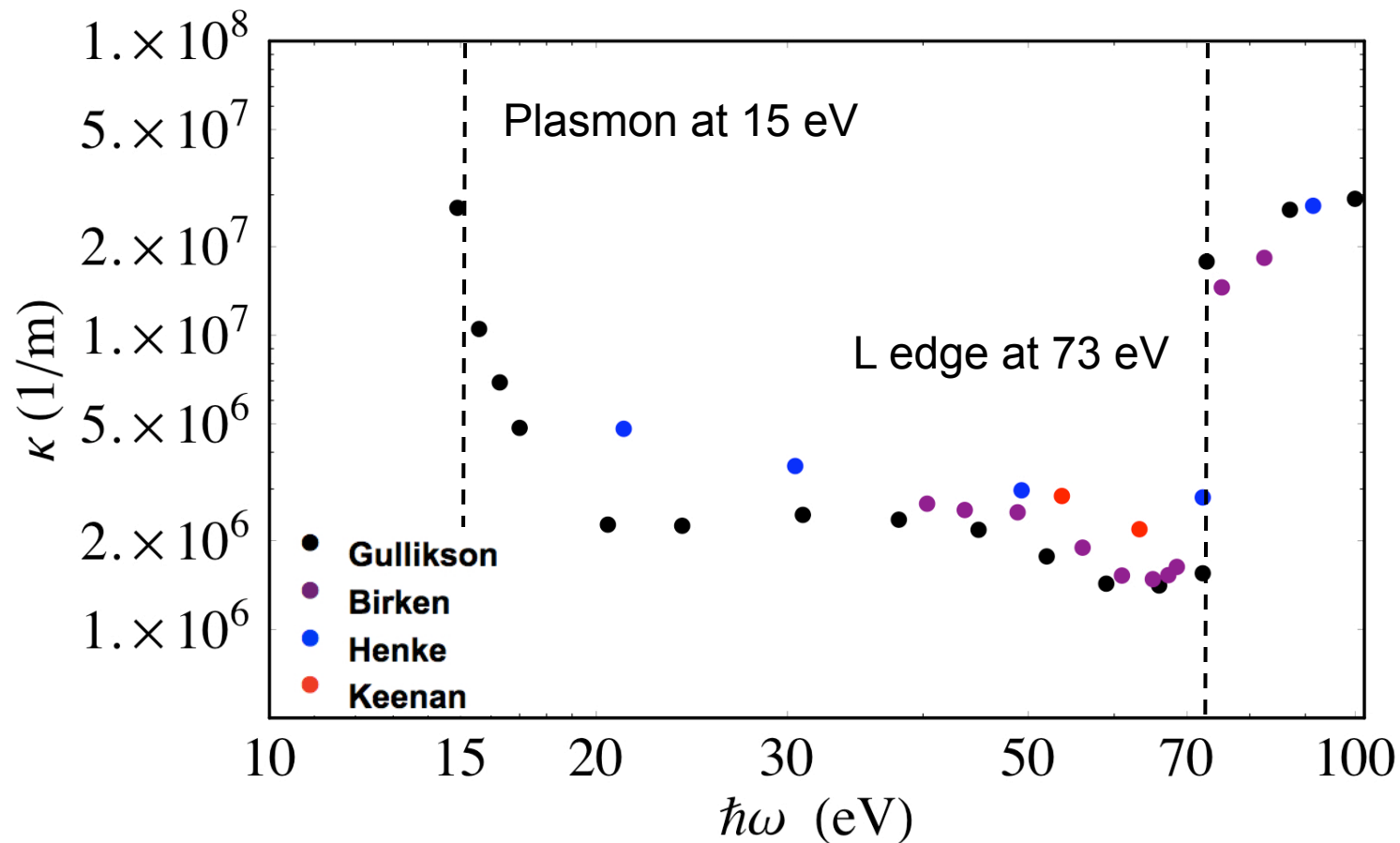
- **Gullikson** E.M. Gullikson, P. Denham, S. Mrowka, J. Underwood, Phys. Rev. B 49, 16283 (1994).
- **Birken** Birken, Jark, Kunz and Wolf, *Nucl. Instrum. Methods Phys. Res. A* 253 166 (1986).
- **Henke** B.L. Henke, E.M. Gullikson, J.C. Davis, Atom. Data Nucl. Data Tables 54, 181 (1993).
- **Keenan** R. Keenan, C. Lewis, J. Wark, E. Wolfrum, J. Phys. B 35 L447 (2002).

**Differences between the data sets are significant**

**Experiments must either carefully account for oxidation, or eliminate it**

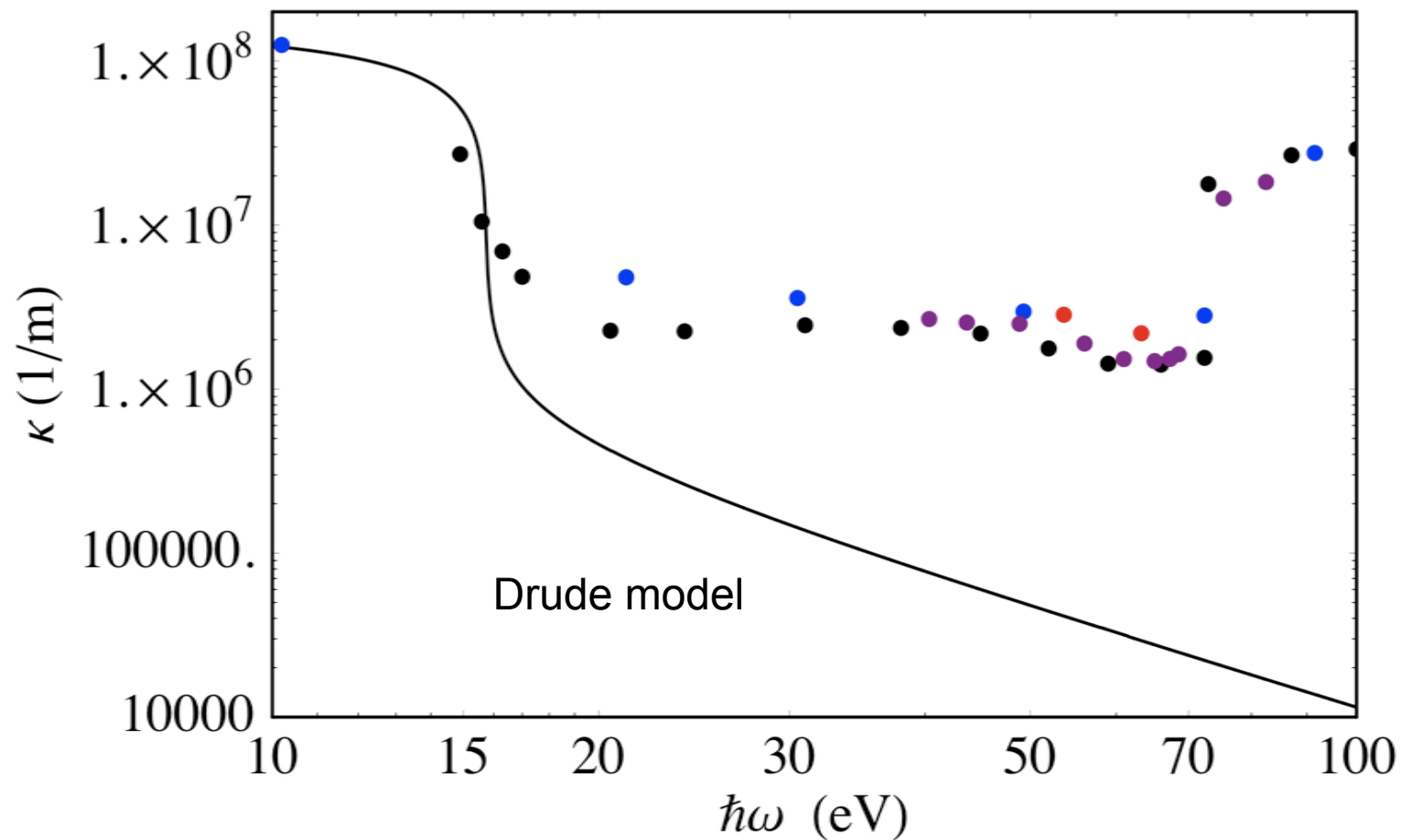


The data ranges from the plasmon energy to the L edge and beyond



Modest differences in absorption but large differences in transmission

Although a free electron metal, the Drude model grossly underestimates the absorption in aluminum



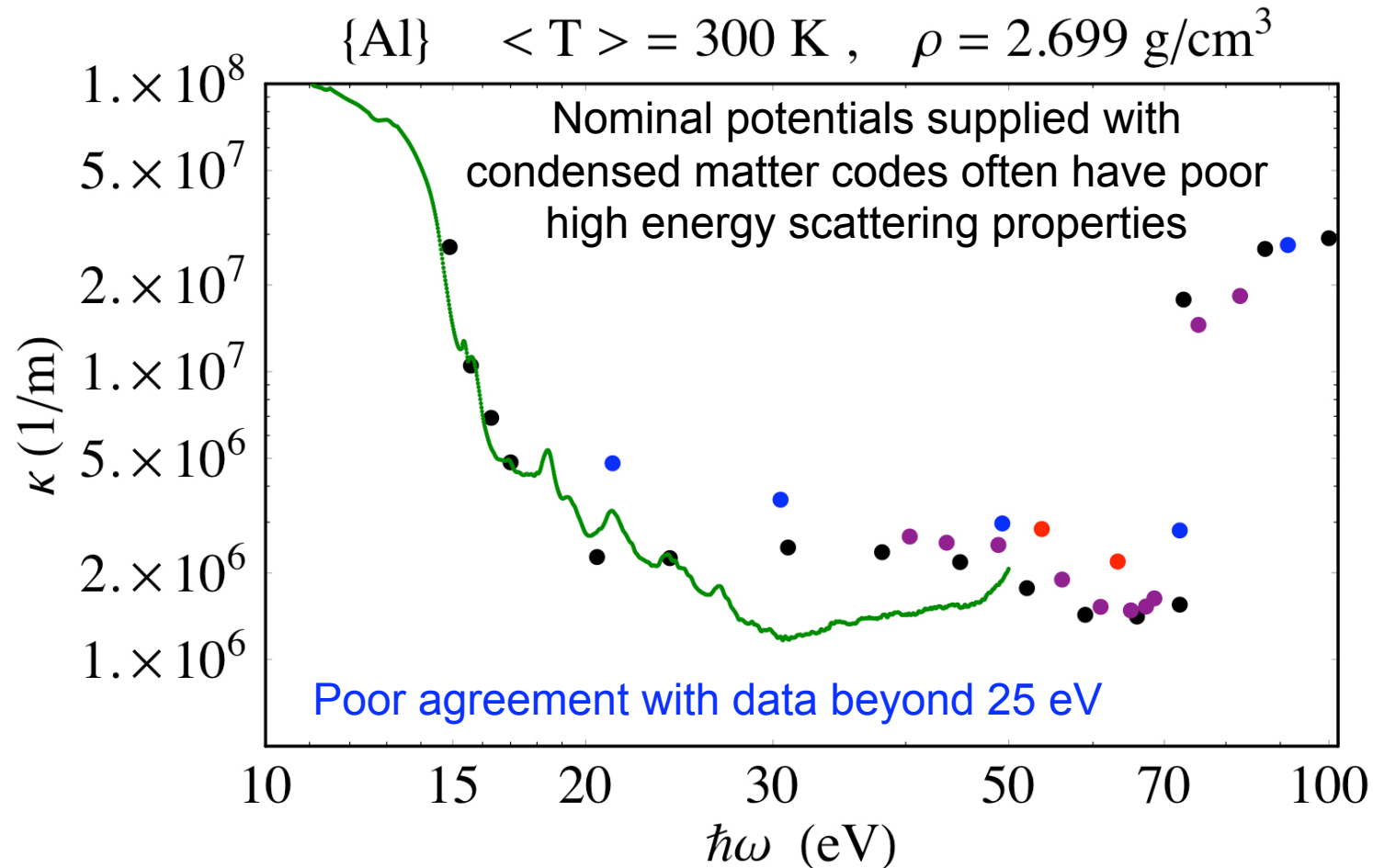
Simple atomic cross section calculations do much better at higher energies



## We calculate the absorption in fcc aluminum with electronic structure methods

- **Density functional theory (DFT)**
  - DFT calculations with VASP (Vienna *ab initio* simulation program)
    - Projector Augmented Wave (PAW) potentials
  - Kubo-Greenwood for transport properties (no local field corrections)
  - Full inverse dielectric calculations (local fields/Umklapp processes included)
    - Adler (1962), Wiser (1963)
  
- **GW methods** ( $G$ : Green's function,  $W$ : Dynamically screened Coulomb operator; much better excited states; accurate band gaps in semiconductors)
  - Also with VASP, at the level of  $G_0W_0$  (single pass, using DFT wavefunctions) and  $GW_0$  (iterative convergence on  $G$ , no update on  $W$ )
  - With and without local field corrections

## Our initial attempts to calculate the XUV absorption with DFT were disappointing



A new potential was developed with careful attention to the high energy scattering properties

## We first compute the dielectric and absorption properties without local field corrections

The usual approach (Kubo-Greenwood) to calculating the dielectric:

Assume  $\phi^{ext} = \phi^{ext}(\mathbf{q}, \omega) \exp[i(\mathbf{q} \cdot \mathbf{r} - \omega t)]$

Calculate the response  $\phi^{tot} = \phi^{ext} + \phi^{ind}$

assuming  $\phi^{ind} = \phi^{ind}(\mathbf{q}, \omega) \exp[i(\mathbf{q} \cdot \mathbf{r} - \omega t)]$

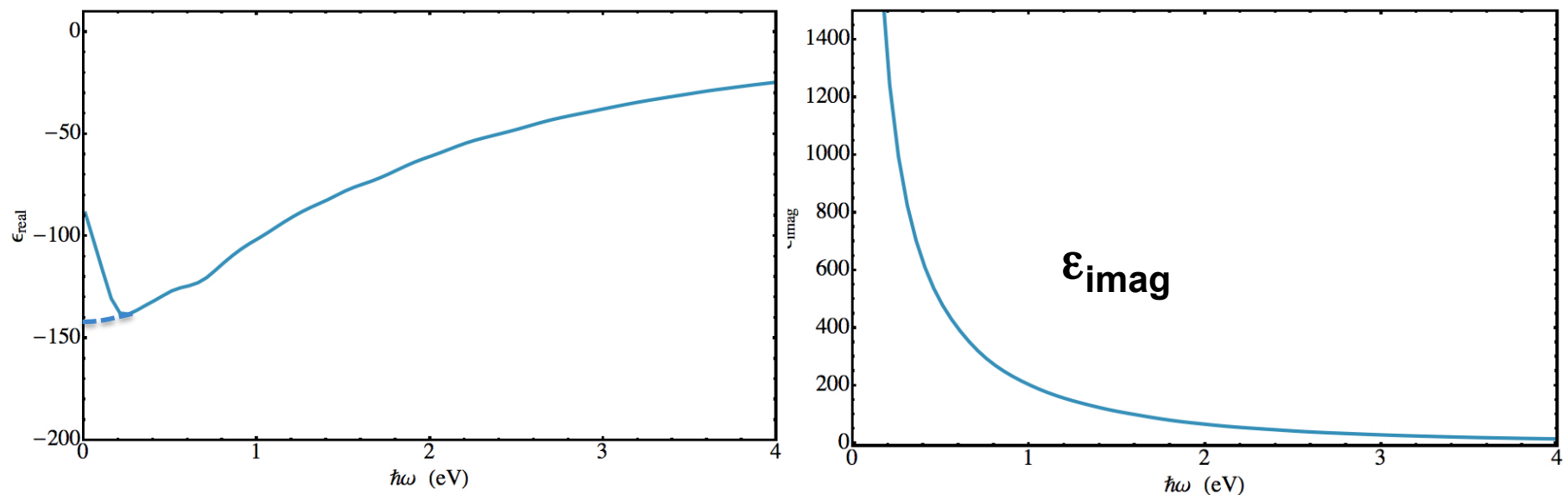
For optical properties ( $\mathbf{q} = 0$ )

$$\sigma_{\mathbf{k}}(\omega) = \frac{2\pi e^2 \hbar^2}{3m^2 \omega \Omega} \sum_{\alpha=1}^3 \sum_{j=1}^N \sum_{i=1}^N (F(\varepsilon_{i,\mathbf{k}}) - F(\varepsilon_{j,\mathbf{k}})) \left| \langle \Psi_{j,\mathbf{k}} | \nabla_{\alpha} | \Psi_{i,\mathbf{k}} \rangle \right|^2 \delta(\varepsilon_{j,\mathbf{k}} - \varepsilon_{i,\mathbf{k}} - \hbar\omega),$$

with other optical properties derived through Kramers-Krönig relations

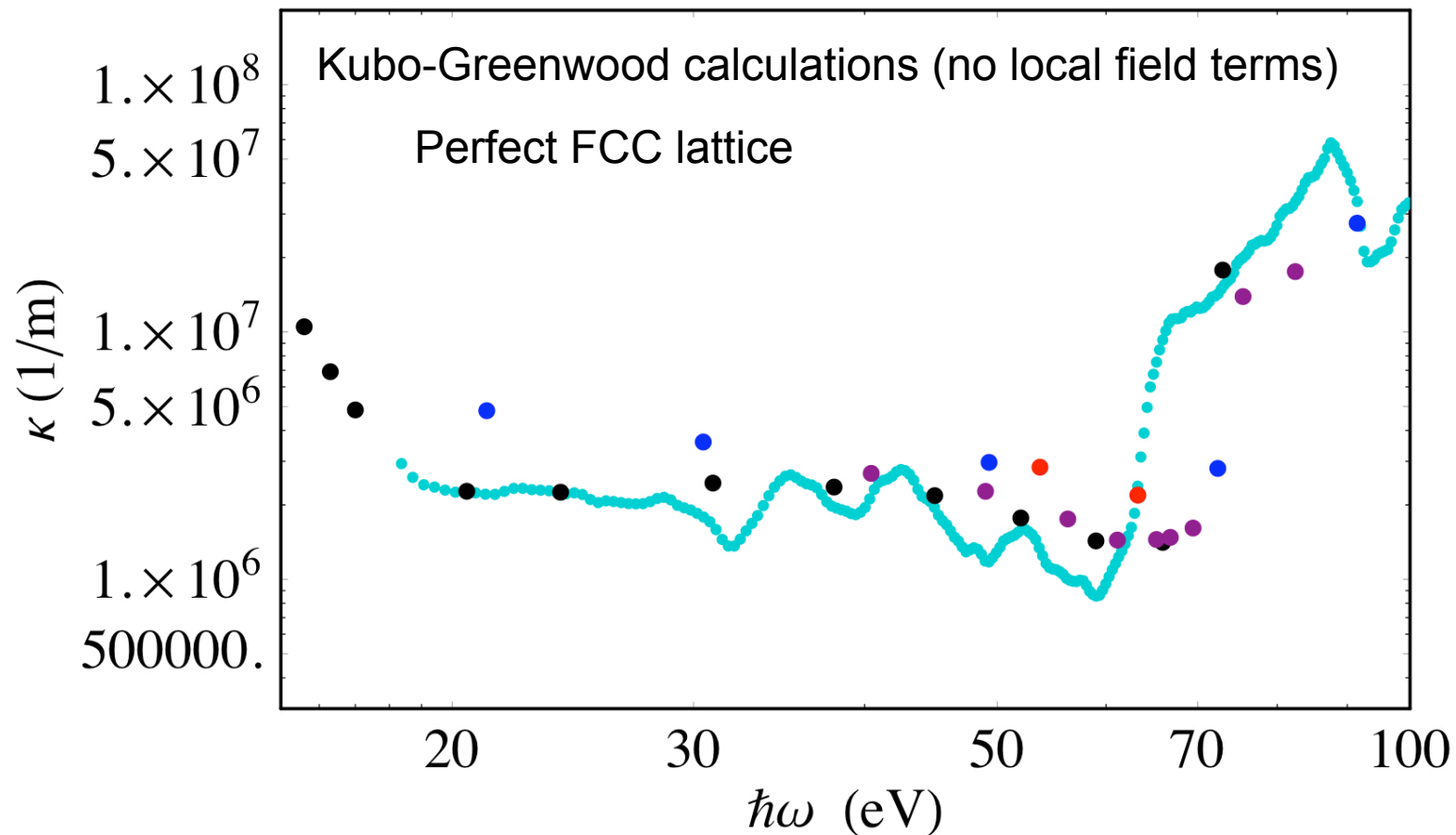
**This approach has been very successful for dc and lower energy (visible light) optical properties in simple metals**

■ **Aluminum at 5.4 g/cc and 30000K**



**These are key quantities in pyrometry analysis and readily calculated with QMD/DFT**

**Density functional calculations of the XUV absorption  
lie below the data and give an L edge ~ 10 eV too low**





## Deriving the dielectric with local field effects included is considerably more involved

Recall that in periodic lattices (Bloch Theory), momentum conservation requires

$$\mathbf{k} \rightarrow \mathbf{k} + \mathbf{q} \quad \text{OR} \quad \mathbf{k} \rightarrow \mathbf{k} + \mathbf{q} \pm n\mathbf{K}$$

where  $\mathbf{k}$  refers to the crystal momentum of an electron at point  $\mathbf{k}$  in the first Brillouin zone and  $\mathbf{K}$  is a reciprocal lattice vector (e.g.  $2\pi/L$ ).

In general then, an external field with wavevector  $\mathbf{q}$  will induce

$$\phi^{ind} = \sum_{\mathbf{K}} \phi^{ind}(\mathbf{q}, \mathbf{K}, \omega) \exp[i(\mathbf{q} + \mathbf{K}) \cdot \mathbf{r} - i\omega t]$$

$\rightarrow \epsilon^{-1}(\mathbf{q} + \mathbf{K}, \mathbf{q} + \mathbf{K}', \omega)$

Local field contributions, Umklapp processes

**A much more complicated object (Adler, Wiser)**

## The dielectric with local field corrections is the solution to an integral equation for $1/\epsilon$

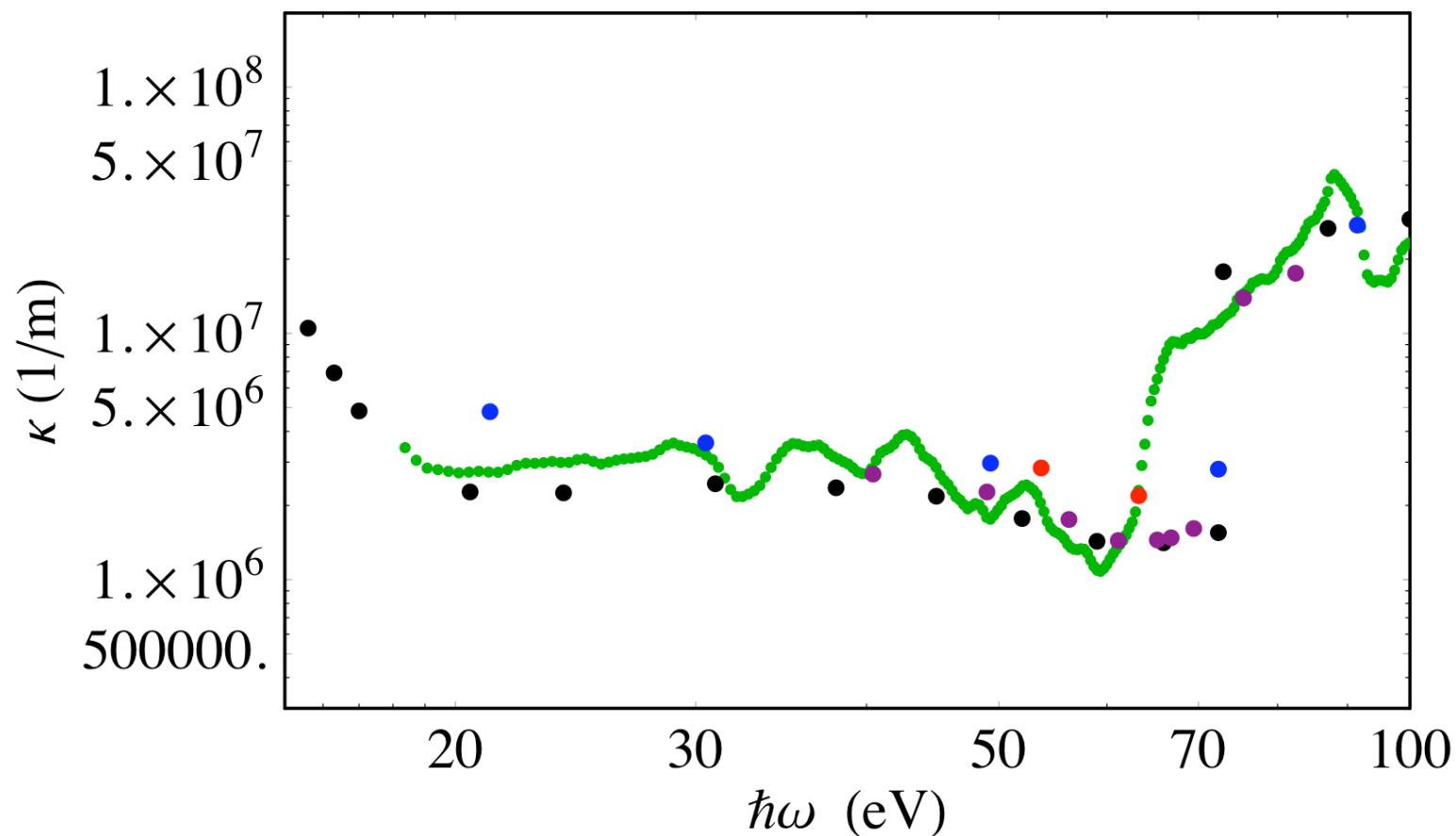
$$\epsilon^{-1}(\mathbf{q} + \mathbf{K}, \mathbf{q} + \mathbf{K}', \omega) = \delta_{\mathbf{K}, \mathbf{K}'} + \sum_{\mathbf{K}''} \frac{G(\mathbf{q} + \mathbf{K}, \mathbf{q} + \mathbf{K}'', \omega)}{|\mathbf{q} + \mathbf{K}''|^2} \epsilon^{-1}(\mathbf{q} + \mathbf{K}'', \mathbf{q} + \mathbf{K}', \omega)$$

Where

$$G(\mathbf{q} + \mathbf{K}, \mathbf{q} + \mathbf{K}'', \omega) =$$

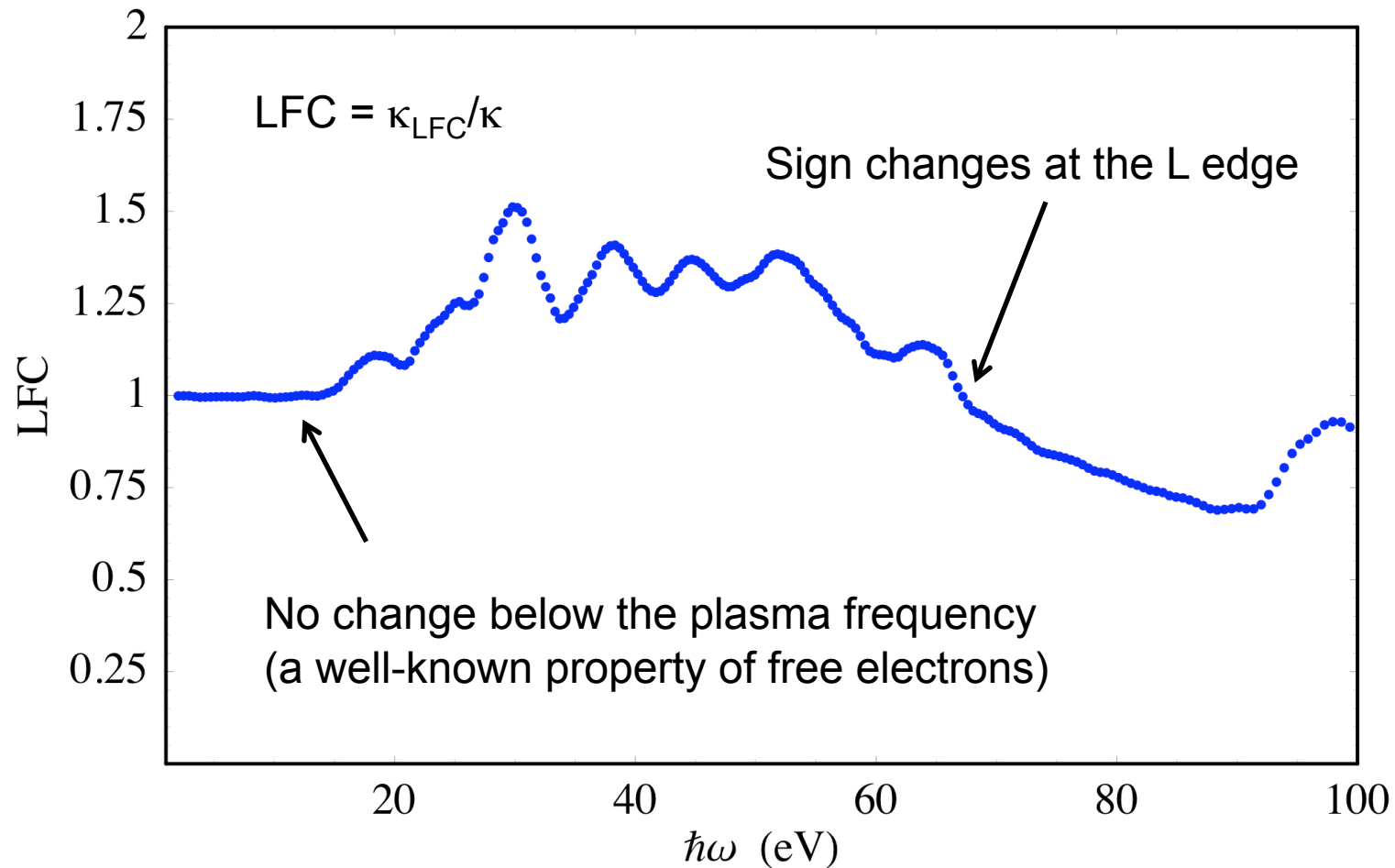
$$\frac{4\pi e^2}{V} \sum_{l l' \mathbf{k}} \frac{\langle l \mathbf{k} | \exp(-i\mathbf{K} \cdot \mathbf{r}) | l' \mathbf{k} + \mathbf{q} \rangle \langle l' \mathbf{k} + \mathbf{q} | \exp(i\mathbf{K}'' \cdot \mathbf{r}) | l \mathbf{k} \rangle [F(\epsilon_{l \mathbf{k}}) - F(\epsilon_{l' \mathbf{k} + \mathbf{q}})]}{\hbar\omega + \epsilon_{l \mathbf{k}} - \epsilon_{l' \mathbf{k} + \mathbf{q}}}$$

**DFT with local field corrections improves the agreement with data but does nothing for the L edge**

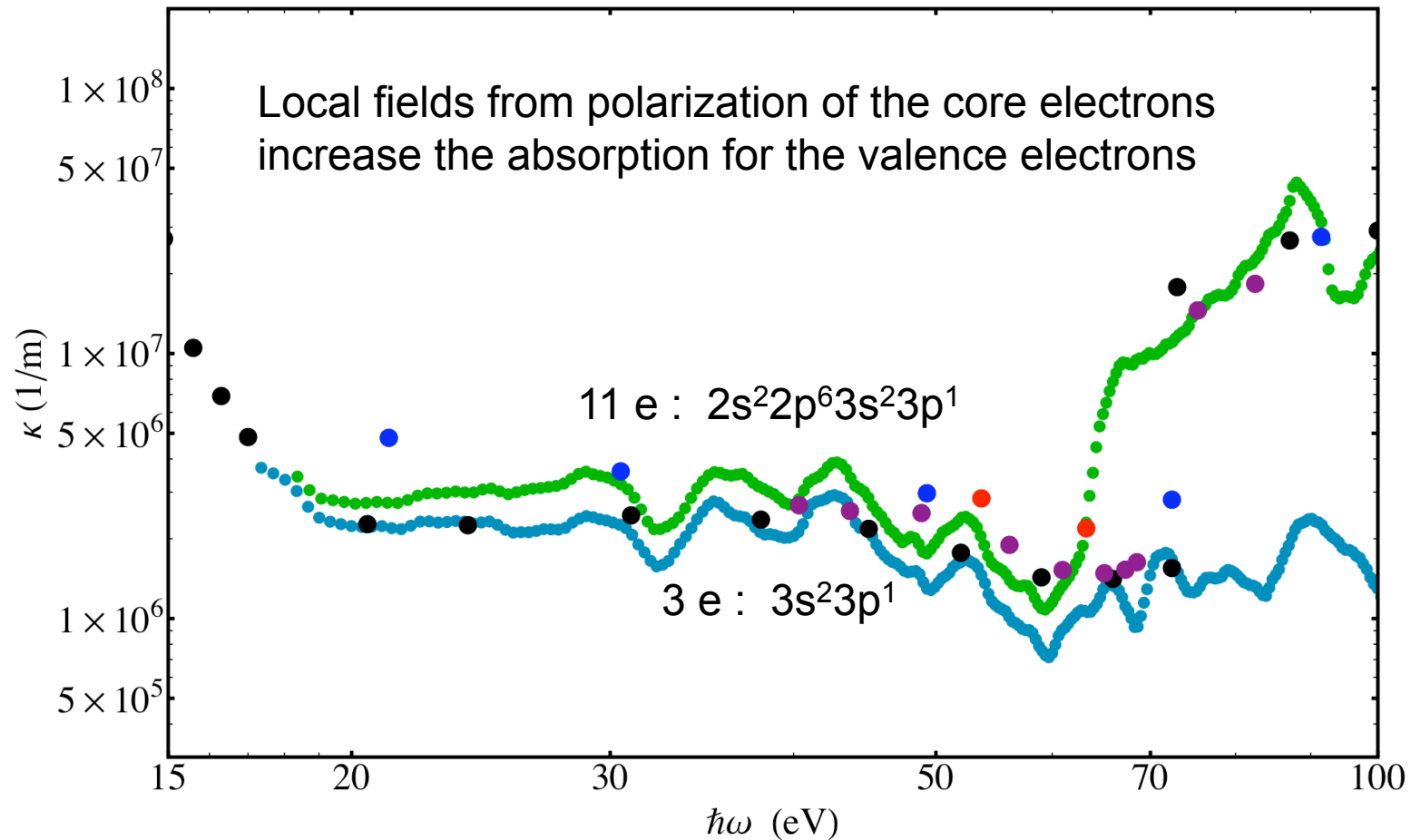


Inaccurate prediction of the L edge is expected with DFT

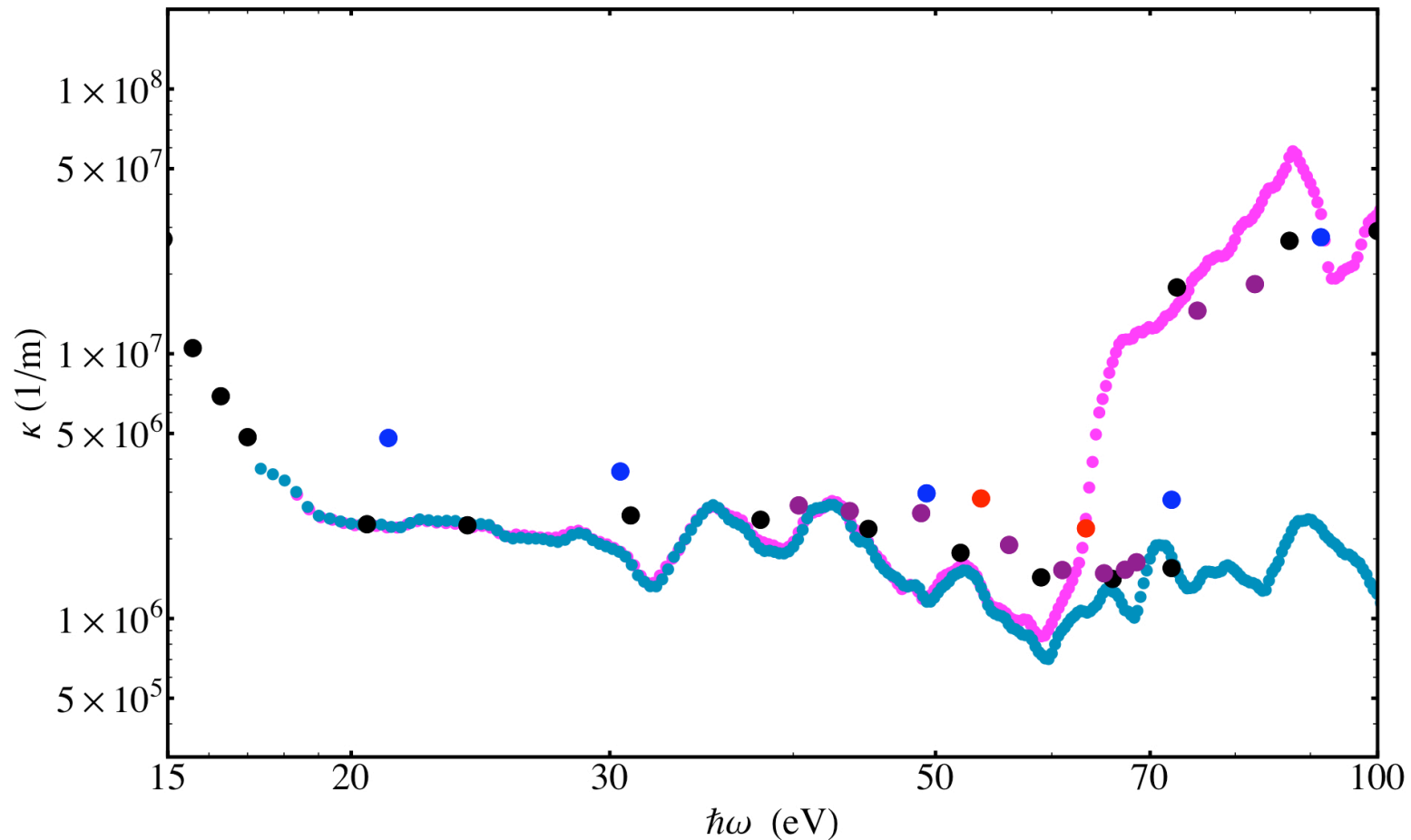
## The local field effects make a significant contribution to the absorption



## Core electrons are important when local fields are included



**If we ignore the local field corrections, the core electrons play no role below the L edge**



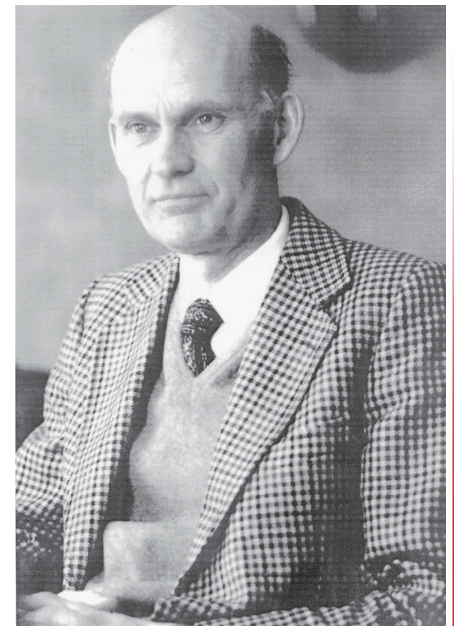
## Hedin's GW approximation

$$(T + V - \varepsilon_{\mathbf{k}}) \psi_{\mathbf{k}}(\mathbf{r}) + \int d^3\mathbf{r}' \Sigma(\mathbf{r}, \mathbf{r}', \varepsilon_{\mathbf{k}}) \psi_{\mathbf{k}}(\mathbf{r}') = 0$$

where the self energy operator  $\Sigma$  is given by

$$\Sigma(\mathbf{r}, \mathbf{r}', \omega) = \frac{i}{4\pi} \int_{-\infty}^{\infty} e^{i\omega'\delta} G(\mathbf{r}, \mathbf{r}', \omega + \omega') W(\mathbf{r}, \mathbf{r}', \omega') d\omega'$$

and where  $\mathbf{G}$  is the single particle Green's function  
and  $\mathbf{W}$  is the dynamically screened Coulomb interaction.

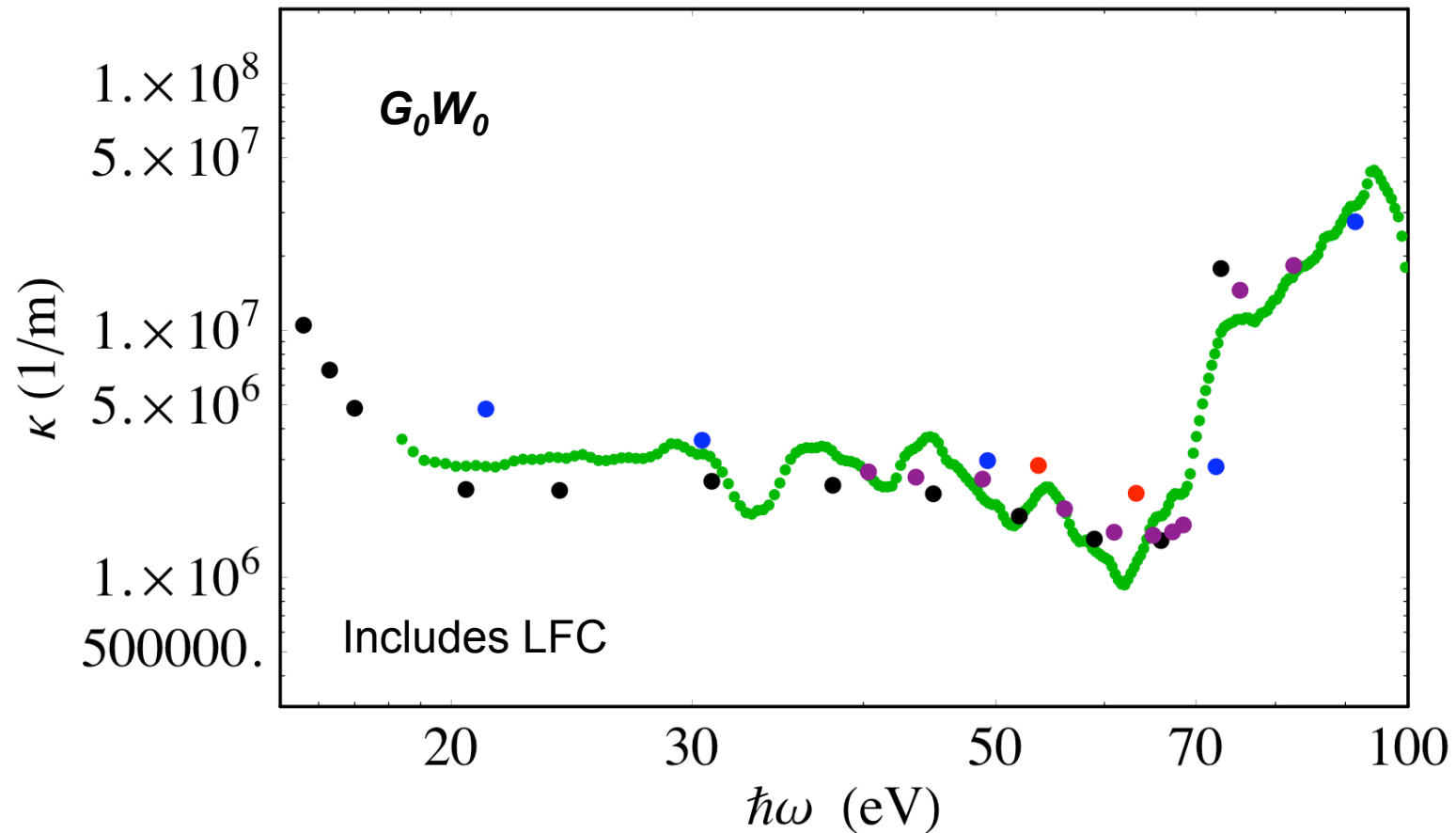


Lars Hedin

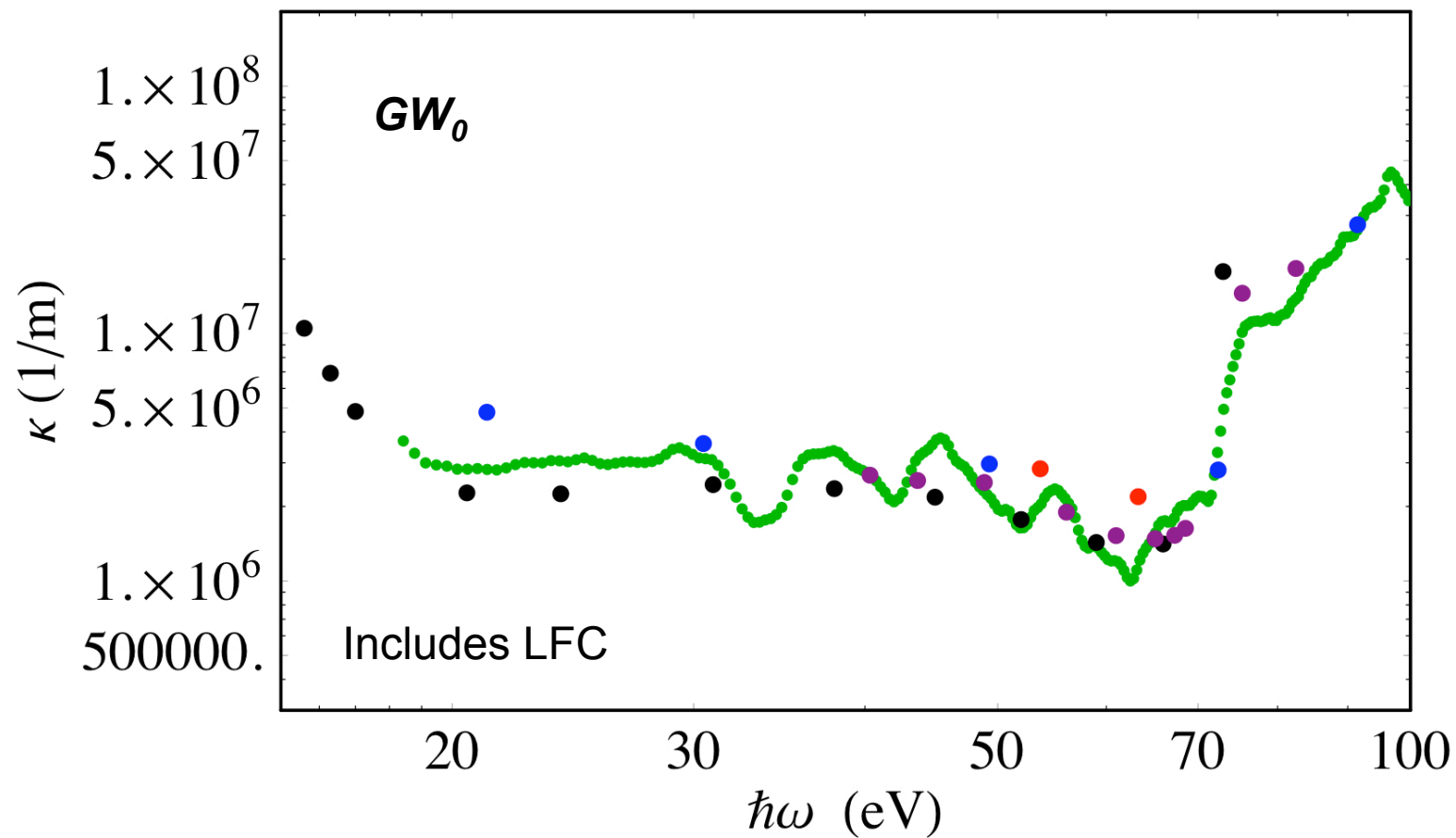
This dramatically improves over DFT in the calculation of  
band gaps and band widths (much more expensive)



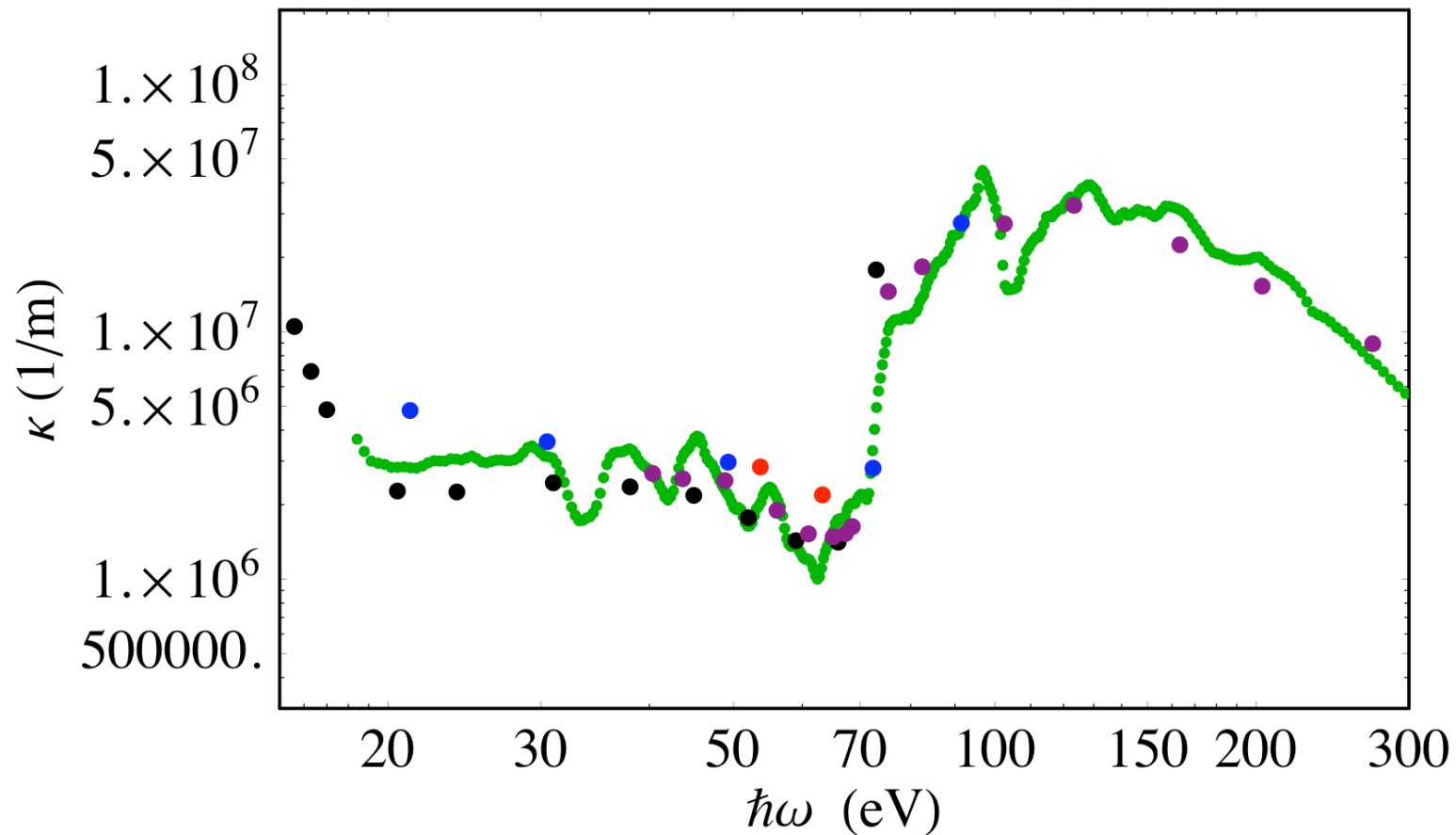
In the  $G_0W_0$  approximation, DFT eigenvalues and eigenfunctions are used to construct  $G$  and  $W$



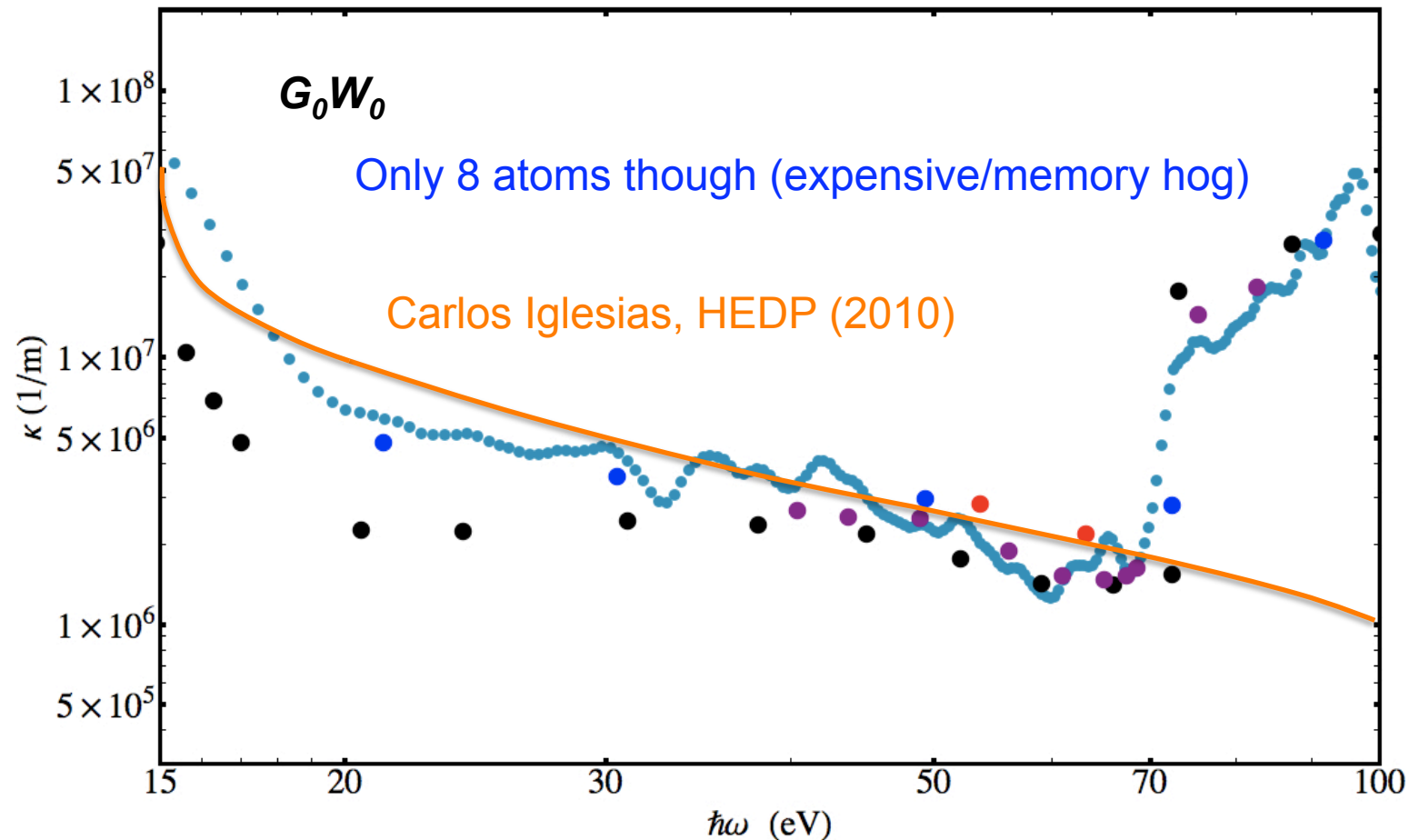
## Iterating on the eigenvalues and eigenfunctions in $G$ converges to the measured L edge



**We find good agreement with absorption data out to  
300 eV**

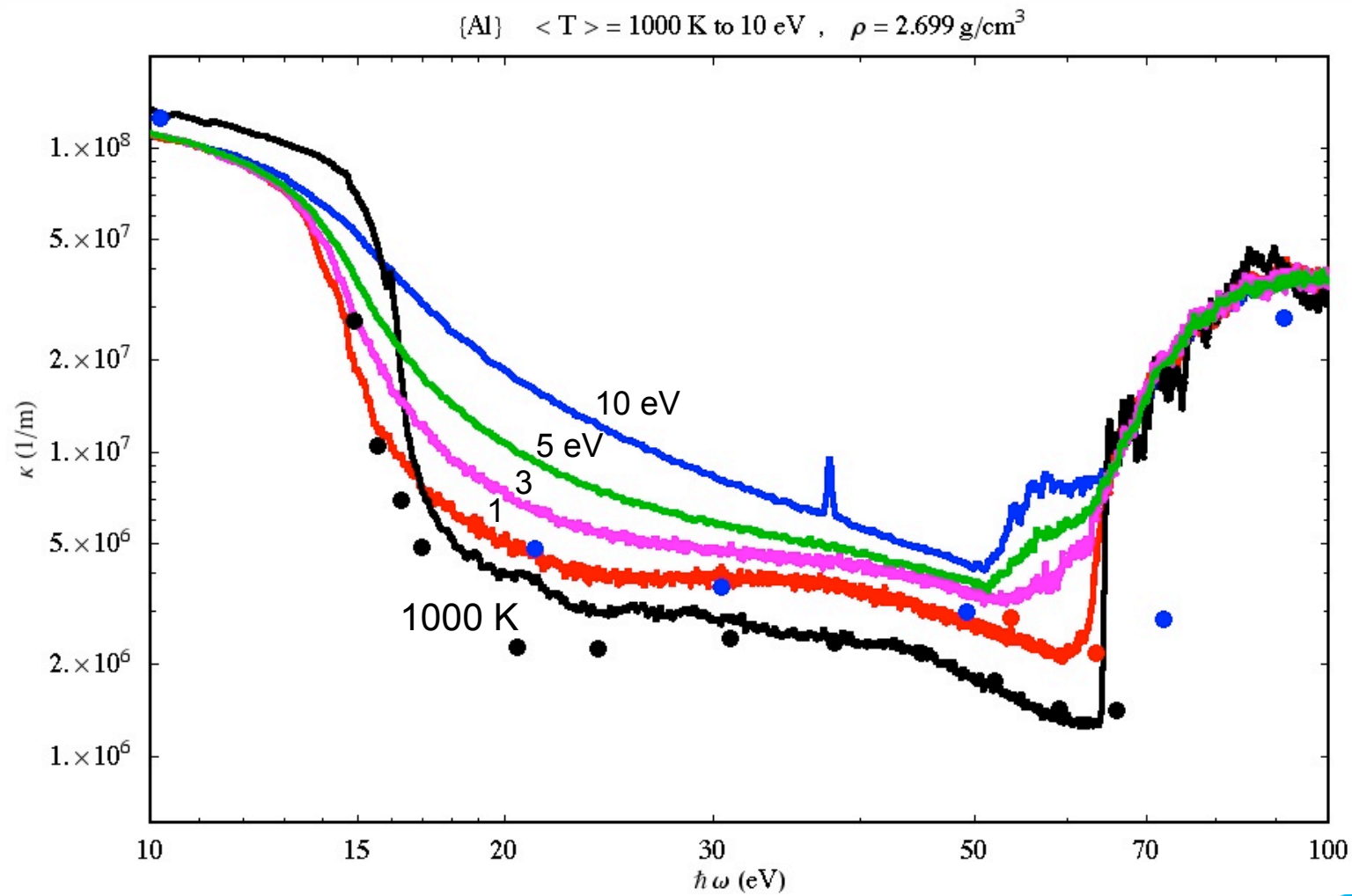


## GW calculations with thermal configurations show enhanced lower energy absorption



Thermal configurations matter little beyond 50 eV

## Finally, some warm dense aluminum





## Summary

- **We have explored the utility of electronic structure methods in calculating absorptions beyond the plasma frequency.**
- **Even with good potentials, DFT without local field corrections is good to within about a factor of two, and edges can be several eV off.**
- **With LFC, DFT gets the absorption generally pretty well, but edges would need to be corrected.**
- ***GW* methods, with core electrons and local field corrections, do very well. Thermal configurations are important at lower energies.**